# Recent Developments in Hot-Gas Desulfurization

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## Abstract

High-temperature removal of reduced sulfur species ($H_2S$, COS, $CS_2$, etc.) from synthesis gas produced by gasification/reforming of carbonaceous feedstocks is an attractive option from process and economic standpoints to conventional amine-based cold cleanup processes. This removal is accomplished with either disposable (e.g., calcium oxides) or regenerable (e.g., zinc oxide) metal oxide sorbents in a suitable reactor configuration. To be effective, the use of disposable sorbents for high-temperature gas desulfurization is limited to *in situ* injection into a gasifier for bulk sulfur removal followed by a polishing bed downstream to reduce sulfur levels to less than 20 parts per million by volume (ppmv). This paper is focused on the regenerable sorbents and provides a review of the current status of various research and development (R&D), pilot-scale, and commercial demonstration projects primarily in the United States. An attempt was made to include research done in other countries, mainly Korea, China, Japan, and Turkey. The review focuses on the activities carried out over the past 3 years (after the Third International Gas Cleaning Conference in 1996).

**Keywords:** sulfur, desulfurization, sorbent, gasification, regenerable, zinc titanate, hydrogen sulfide, carbonyl sulfide, synthesis gas, purification, sulfur recovery.

## 1. Introduction

The primary impetus for research on high-temperature sulfur removal processes has been the development and commercialization of the integrated gasification combined cycle (IGCC) technology. In an IGCC system, a carbonaceous feedstock, such as coal, petroleum coke, or biomass, is gasified under pressure to produce a fuel gas (also referred to as “synthesis gas”), which is desulfurized prior to combustion in a turbine

to generate electricity or used for coproduction of Fisher-Tropsch (F-T) fuels or chemicals. Although projected capital costs of IGCC plants are higher ($1,200 per kW) than those of conventional natural gas burners, IGSC plants' high thermal efficiency (up to 47% as now demonstrated commercially (DOE 1999)), modular design, and superior environmental performance are major advantages over conventional coal-to-electricity processes. Hot-gas cleaning is a vital component of IGCC plants and consists of removal of particulate matter and gaseous contaminants (sulfur, chlorine, ammonia, and alkali vapors). This review paper focuses on removal of sulfur species from synthesis gas using primarily regenerable sorbents.

The high-temperature sulfur removal using a regenerable metal oxide (MeO), where Me is a suitable metal, is carried out in a two-reactor system consisting of a desulfurizer and a regenerator:

$MeO + H_2S = MeS + H_2O$ (Removal of $H_2S$ in a desulfurizer)
$MeS + O_2 = MeO + SO_2$ (Regeneration of sulfided sorbent in a regenerator).

The main criteria for a metal oxide to be suitable for this process include: reactivity with both $H_2S$ and COS at desired temperatures and pressures; favorable thermodynamics to reduce the sulfur level to a desired value; its stability in reducing and oxidizing conditions; and easy regeneration under oxidizing conditions without formation of undesirable side products such as metal sulfates.

## 2. Desulfurization in the Unites States

Prior research using metal oxide sorbents has been extensively reported (Gangwal 1991; Gupta and Gangwal 1992; Thambimuthu 1993; Gangwal 1996; Mitchell 1998; Atimtay and Harrison 1998). This research and development work has been spearheaded by the United States Department of Energy's (DOE's) Federal Energy Technology Center (FETC) since 1975.

The majority of the sulfur removal research has been focused on zinc oxide-based sorbents because of their favorable thermodynamics, good kinetics for desulfurization and regeneration, and good stability under reducing and oxidizing conditions. Mixed-metal oxide sorbents combining zinc oxide with a secondary oxide (e.g., iron, titanium, or nickel oxide) have also been investigated to either enhance desired effects or control deleterious ones. Several mixed-metal oxide sorbents, including EX-SO3 zinc titanate (containing zinc oxide and titanium dioxide), Z-Sorb (zinc oxide and nickel oxide on

a proprietary matrix), and RVS-1 (ZnO on a patented matrix), are being tested at pilot- to demonstration-scale. Recent results of these tests are reported here.

After selection of a suitable sorbent composition, the next vital piece of a gas cleanup system is the process reactor design. A two-reactor system is necessary due to the cyclic nature of the process. DOE/FETC sponsored extensive reactor design studies. Early reactor designs involved fixed-bed reactors. However, the highly exothermic and difficult to control regeneration reaction and formation of undesirable metal sulfates during regeneration forced the investigation of alternate designs, such as moving beds and fluidized beds. General Electric (GE) developed a moving-bed desulfurization system that employed 3 to 4 mm diameter sorbent pellets (Ayala et al. 1995). GE designed and constructed a 25 MW commercial prototype of this system for a demonstration at Tampa Electric Company's IGCC Clean Coal Technology Demonstration plant in Tampa, FL. A 59,000 kg (130,000 lb) batch of Z-Sorb sorbent (developed and supplied by Phillips Petroleum Company) was ordered for this demonstration. Because of incompatibility of component designs and unexpectedly lower gas temperatures from the Texaco gasifier system, the hot-gas desulfurizer has not been placed into operation.

Fluidized-bed reactors may be the most prudent choice for conducting hot-gas desulfurization. They have several advantages over fixed- or moving-bed reactors, including excellent gas-solid contact, rapid kinetics, the ability to handle particles in gas, and the ability to control temperature during highly exothermic reactions. However, the sorbent must be highly reactive and attrition-resistant for a fluidized-bed reactor to work successfully. Sierra Pacific Power Company's Piñon Pine IGCC Clean Coal Technology Demonstration plant uses a fluidized/transport-bed reactor system for hot-gas desulfurization. This transport reactor system was developed by the Kellogg, Brown and Root (KBR) Company. A process description is provided later in this paper.

The Phillips Petroleum Company developed a fluidized-bed version of its patented Z-Sorb sorbent (Khare et al. 1996). This sorbent was prepared by spray drying or granulation techniques. Phillips provided a 60,000 lb batch of Z-Sorb sorbent for a demonstration at Piñon Pine. During initial startup in December 1997, the sorbent exhibited excessive attrition, and as a result, further testing was discontinued (Demuth and Smith, 1998).

Working with DOE/FETC, Research Triangle Institute (RTI) researchers have conducted the zinc titanate sorbent development over the past 10 years (Gupta et al.

1996). This work has led to the successful development of a number of zinc titanate sorbents prepared by both granulation and spray drying. A number of life cycle tests have been performed on a zinc titanate sorbent, named ZT-4, which was patented by RTI and DOE (Gupta et al. 1993) to demonstrate its long-term chemical reactivity and attrition resistance. These tests were conducted using synthesis gas produced directly from coal gasifiers at three pilot plant sites: Enviropower in Finland, DOE/FETC at Morgantown, USA, and Coal Technology Development Division (CTDD) in England. The superior performance exhibited by the ZT-4 sorbent used in fluidized-bed reactors during these tests is reported in Gupta et al. (1996).

Figure 1 shows a schematic diagram of the patented KBR transport reactor system. As outlined in Henningsen et al. (1997), the transport reactors have significant advantages over conventional fluidized-bed reactors, including:

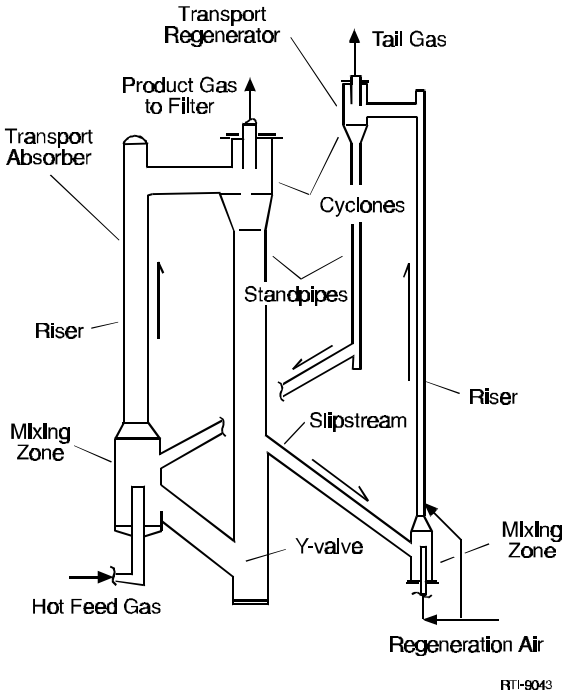


**Figure 1. Schematic of Piñon Pine gas desulfurization system.**

- The sorbent inventory requirements are much smaller, because gas velocities are about 20 to 40 times higher and riser gas-to-solid volume ratios are much smaller.
- The time of sorbent exposure to a reactive gas environment is on the order of 1 to 2 s during both absorption and regeneration.
- A transport reactor can handle a feed gas containing fines not captured by the upstream cyclone.
- Only a slipstream of circulating solids is used for regeneration; hence, control of temperature rise is easier and no diluent is required to absorb the heat.
- The amount of sulfur absorbed and regenerated per cycle is between 2 and 4 wt%, thus eliminating the need for a high sulfur capacity sorbent.

In this system, both the desulfurization and regeneration are carried out in a transport mode, with provision for sorbent transfer between the two reactors. It should be noted that the Piñon Pine transport desulfurization system is used as a polishing bed to remove 400 to 600 ppmv of $H_2S$ in the synthesis gas down to <20 ppmv. The KRW

fluidized-bed gasifier used in the Piñon Pine IGCC employs limestone for *in situ* bulk sulfur capture.

For successful operation of the transport reactor system, the sorbent must meet certain specifications. As shown in Figure 2, for transport reactor applications, a sorbent:

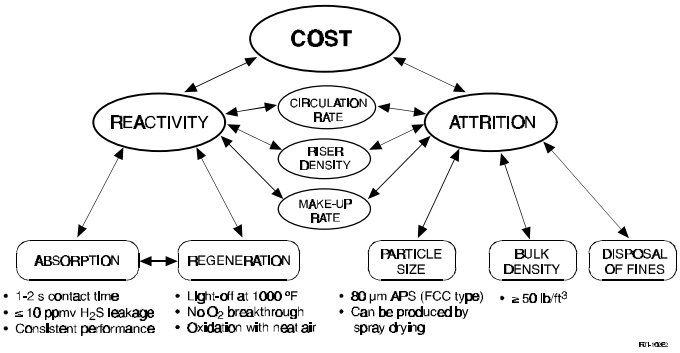


**Figure 2. Criteria for commercial sorbent selection.**

- Must possess and maintain high chemical reactivity for removing sulfur species from synthesis gas within 1 to 2 seconds of residence time
- Must maintain an attrition rate below design specifications
- Must be regenerable using neat air to maintain cyclic operation
- Must possess good flow characteristics
- Should be competitively priced.

While ZT-4 sorbent exhibited excellent performance for bubbling fluidized-bed systems, it suffered attrition problems when tested under transport mode. This prompted development of a spray-dried version of the sorbent to improve its attrition resistance. As reported (Gupta et al. 1996), initial efforts to produce suitable sorbents for this application by spray drying led to development of the CMP-107 sorbent. The CMP-107 sorbent was manufactured by Contract Materials Processing (CMP), Inc., of Baltimore, MD. Pilot-scale testing of this sorbent by KBR indicated that the sorbent readily removed $H_2S$ to <5 ppmv (the analytical detection limit), but its attrition rate was about twice the target value that KBR required in the transport reactor design for the Piñon Pine plant (Gupta et al. 1996a).

Using the guidelines on sorbent specifications (Figure 2), research efforts were focused on improving the attrition resistance of spray-dried zinc titanate sorbents while maintaining their chemical reactivity, sulfur capacity, and regenerability. RTI and Intercat Development, Inc., of Sea Girt, NJ, jointly worked on the development and commercialization of the spray-dried zinc titanate sorbents. Intercat is a commercial catalyst manufacturer specializing in spray drying FCC additives for petroleum refineries. The research efforts led to a zinc titanate formulation, designated as EX-S03 (Gupta et al. 1997). As a prequalification requirement, a 450 kg (1,000-lb) batch of

this material was produced in a commercial-scale spray drier to demonstrate the scale-up of the manufacturing process. Details of the composition and the manufacturing process for the EX-S03 sorbent are proprietary to Intercat and RTI, and a patent is pending.

RTI conducted bench-scale tests using their high-temperature, high-pressure (HTHP) sorbent test facility described in Gupta et al. (1998) with the EX-S03 sorbent (from the 450 kg batch) to determine its long-term chemical reactivity and mechanical strength.

Following successful bench-scale tests, testing of the EX-S03 sorbent was carried out at KBR's transport reactor test unit (TRTU) to determine its suitability for use at the Piñon Pine plant. Two batches of sorbent from the same lot were tested. The first batch was subjected to three sulfidations and two regenerations and then circulated in the cold flow model to study its flow properties and to determine its attrition. The second batch was tested over multiple cycles of absorption and regeneration in order to determine the change in sulfur absorption capacity and attrition characteristics after extended operation.

Pertinent findings KBR's TRTU test were:

- Absorption of $H_2S$ showed essentially no leakage of $H_2S$ (<20 ppmv) in the outlet gas when sorbent was not near saturation and when the inlet $H_2S$ concentration was below 6,000 ppm.
- The sulfur absorption capacity of the fresh sorbent was about 9 wt% at $H_2S$ breakthrough (at 1,000 ppmv in the exit gas), and this did not change with cycles. The sorbent capacity values were confirmed by chemical analysis for sulfide sulfur.
- A temperature of 538° to 650°C (1,000° to 1,200°F) was required to regenerate the sorbent.
- The regeneration over eight cycles was good; there was no $O_2$ breakthrough, and expected peak $SO_2$ concentration indicated that no sulfate was formed. This was confirmed by the chemical analysis of the sorbent.
- The sorbent attrition rate based on feed size distributions, the bed drain, and the amount of filter fines collected at the end of eight cycles indicated that the amount of fines generated was about $7.5 \times 10^{-6}$ lb/lb of sorbent circulated based on the amount of fines below 22 µm. This value was an order of magnitude smaller than any sorbent previously tested in the TRTU. This attrition rate equates to about 4.5 lb/h loss of sorbent at the Piñon Pine desulfurizer based on the solid circulation rate. This is much less than expected and represented a significant performance improvement compared with any previously tested sorbents.

From these verification bench-scale and TRTU testing results, Sierra Pacific Power Company (SPPCo) ordered a 50,000 lb batch of the EX-S03 sorbent from Intercat. A sorbent batch was loaded into the external desulfurizer at Piñon Pine and was successfully circulated without attrition problems. Currently, the sorbent is loaded in the desulfurizer and is awaiting full evaluation with the startup of the Piñon Pine IGCC plant, which is expected to be completed later this year.

A major hurdle, which was overcome, was achieving target mechanical attrition resistance levels to minimize sorbent loss from the desulfurizer. The design specification required an Attrition Index (AI) of below 5 and preferably below 2. The AI was measured by the modified ASTM Test Method D-5757-95, which is described in Gupta et al. (1998). Table 1 compares AI values of materials developed by RTI, RTI-CMP, and RTI-Intercat. The AI of the sorbent batch supplied to SPPCo was 1.4, compared with 4.0 for the previous material. This AI value was independently confirmed by KBR.

**Table 1. Attrition Index for Various Generations of Zinc Titanate Sorbents**

| Material | Description | Attrition index |
|---|---|---|
| ZT-4 | Granulated zinc titanate sorbent | >25 |
| CMP-107 | Earlier spray-dried zinc titanate sorbent developed by RTI-CMP | >25 |
| FCC | Commercial fluid-catalytic cracking catalyst | <5 |
| EX-S03 | Earlier version of zinc titanate material developed by Intercat-RTI and used in bench-scale and pilot-plant testing | 4.0 |
| EX-S03 | Commercial material supplied to SPPCo | 1.4 |

Besides attrition, the sorbent was tested for its chemical reactivity and regenerability in RTI's HTHP bench-scale test facility under test conditions simulating the Piñon Pine operating conditions. Figure 3 shows a typical breakthrough curve plotted with $H_2S$ concentration as a function of sulfur loading for this sorbent at a temperature of 1,000°F (538°C). The sorbent met the $H_2S$ leak and sulfur loading targets.

For the EX-S03 sorbent to initiate regeneration under neat air conditions at 1,000°F or below, a light-off additive was needed. RTI researchers patented a suitable light-off

additive composition (Turk and Gupta, 1999). After initial feasibility tests with the composition, Intercat and RTI jointly developed the additive as a commercial material. Intercat produced a batch of this material, designated as LOA-1, for the Piñon Pine plant.

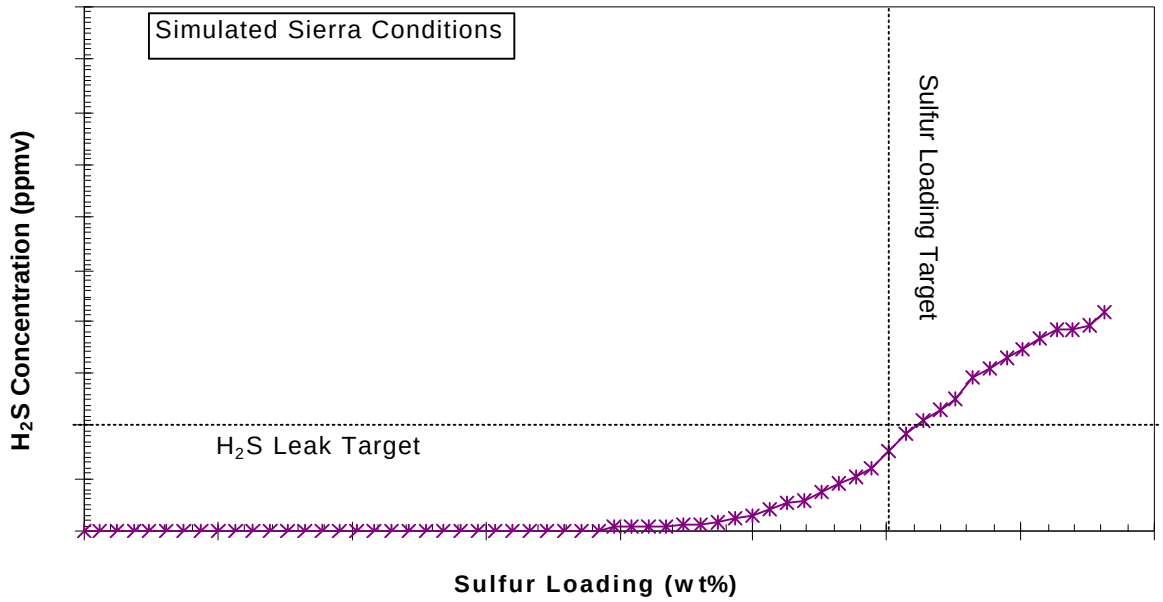


**Figure 3. A typical breakthrough curve for the commercial material supplied to SPPCo.**

In regeneration tests conducted on a mixture of EX-S03 with LOA-1 using a bubbling fluidized-bed, sorbent regeneration was initiated at 800°F (427°C). The maximum temperature achieved was about 1,400°F. These tests clearly indicate that with the LOA-1, regeneration at 1,000°F (538°C) with neat air can be achieved.

In addition to being tested under simulated conditions at RTI, the sorbent was tested at DOE/FETC facilities with real coal gas. Its performance was consistent with the performance observed in RTI testing as described in Gupta et al. (1998). The trace contaminants present in real coal gas, particularly the heavy metals and chlorides, did not affect sorbent performance and were not sequestered on the sorbent. Therefore, this sorbent is expected to function at SPPCo satisfactorily.

A number of other research organizations are pursuing sorbent development work. Hampton University continues to work on improvements to its sorbents prepared by a coprecipitation technique (Jothimurugesan and Gangwal 1999); Phillips Petroleum Company continues to improve its Z-Sorb sorbent; and a paper is presented in this conference describing the results of fixed-bed reactor development efforts by CIEMAT.

A very promising sorbent, RVS-1, is being developed by in-house researchers at DOE/FETC. This sorbent was prepared by United Catalysts, Inc., of Louisville, KY, using a spray drying technique. Initial sorbent testing results are very encouraging. A paper is presented in this conference by Dr. Ranjani Siriwardane describing the development work on this material.

TDA Research of Wheat Ridge, CO, is also working on a sorbent suitable for transport reactor applications but with the express concern of increasing the physical sorbent life. TDA developed a new sorbent structure, calling it a geode, wherein hundreds of hollow points within the material loosely contain the sorbent material. Thus, the sorbent can expand and contract indefinitely without destroying the sorbent structure that surrounds it. TDA has employed differing compositions of zinc ferrite and zinc titinate. Its most recent work has involved the commercial producer Norton Chemical Process Products to produce spray-dried sorbent and its own production method by extrusion and spheronization. Attrition resistance has been greatly improved. However, the suitably reactive formulations have not obtained the target AI of 5. TDA is continuing research by focussing on other techniques, such as alternative spray-drying methods, higher firing temperatures, different extrusion/size reduction techniques, and sorbent activation procedures (Copeland et al. 1999).

Dr. James Swisher of E&A Associates is also pursuing sorbent development. The Illinois State Geological Survey has recently completed fluidized-bed testing of a sample of Dr. Swisher's zinc titanate sorbent from a spray-dried, commercially produced 38 kg (85 lb) batch by the Engelhard Corporation. Although the prebreakthrough $H_2S$ concentration was about 50 ppmv, efforts are continuing to optimize a regeneration ignition material and to improve the sorbent's effectiveness. Testing of this material may be done in the KBR's TRTU later this year.

Besides sponsoring sorbent material development, DOE/FETC is completing the construction of a Gas Process Development Unit (GPDU). The GPDU is able to test both fluid-bed and transport contacting in two transport reactors and two fluid bed reactors and can (a) provide continuous recirculation in either transport or fluid-bed reactor and (b) use a coupled configuration to continuously circulate sorbent between any two reactors.

The GPDU was designed to generate data on the use of solid sorbents to remove sulfur compounds from hot fuel gas. The GPDU is not a combustoer. Both the absorption and regeneration sides of the GPDU have a fluid-bed reactor and a transport reactor,

resulting in four different operation configurations. Figures 4 and 5 show the two fluid-bed and two transport reactor configurations, respectively.

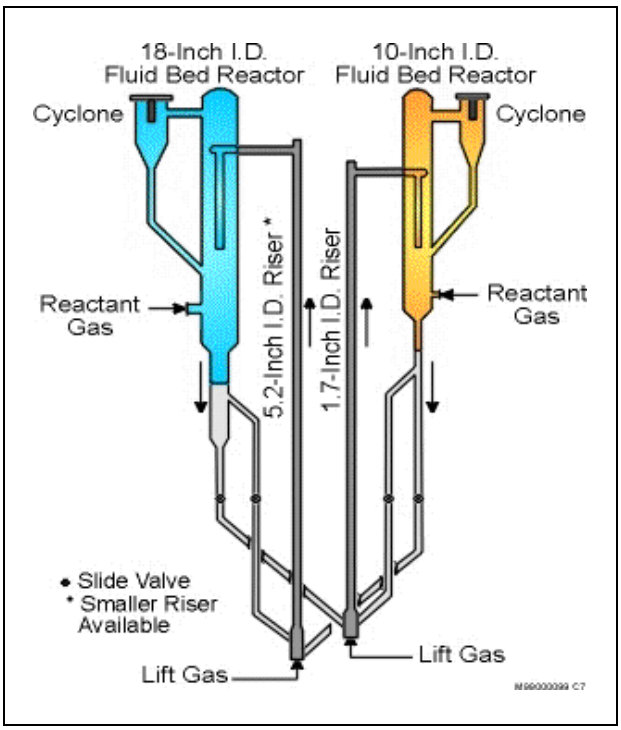


**Figure 4. Two fluid-bed reactor configuration of FETC's GPDU.**

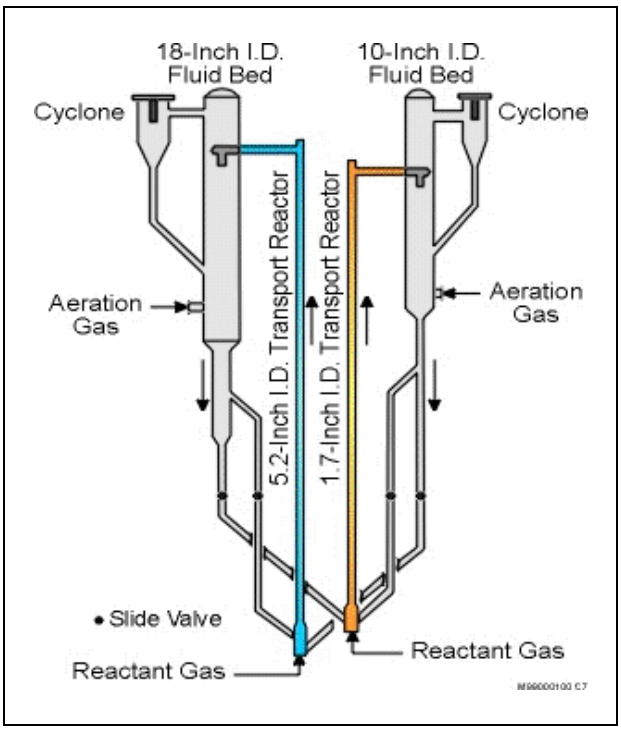


**Figure 5. Two transport reactor configuration of FETC's GPDU.**

The design goals for the GPDU were to define a versatile system that would

- Provide ability to test transport and fluid-bed reactors and sorbents in the same unit
- Demonstrate sorbent suitability over a wide range of parameters
- Generate information on process control for transport and fluidized-bed reactors
- Have process conditions representative of anticipated commercial applications in terms of temperatures, pressures, compositions, gas and solid velocities, and sorbent cycling
- Be configured and sized to produce results scalable to commercial applications.

Some key process parameters are given below:

| | |
|---|---|
| Absorption temperature | 1,000°F to 1,200°F (design) |
| Regeneration temperature | 1,100°F to 1,400°F (design) |
| Absorber-regen differential temp. | 400°F (maximum) at 1,400°F regen |

| | |
|---|---|
| Operating pressure | 400 psia (maximum) |
| Fuel gas flow | 60,000 to 120,000 scfh (typical) |
| $H_2S$ concentration | 0.5 to 1 volume % (typical) |
| Sorbent inventory | 1,000 to 2,000 lb (typical) |
| Circulation rate | 2,000 to 5,000 lb/h (typical) |
| Sorbent size | 50 to 300 microns (typical) |
| Sorbent cycles per day | 50 to 100 (typical) |
| Sorbent flux | 100 lb/s-ft$^2$ (design) |

Although the GPDU was designed for an air-blown, hot-gas desulfurization process development, it can potentially be used for other purposes, such as

- Warm-gas desulfurization process development (temperature of 600° to 800°F)
- Hot or warm gas desulfurization process development for oxygen-blown power systems
- Desulfurization process development for other applications, such as refinery streams, emerging coke and steel processes, and pulp and paper industry
- Removal of other pollutants, such as alkali, ammonia, or HCl
- Development of new catalysts, or configurations, for industrial fluidized-bed or transport reactor processes, such as Fischer-Tropsch synthesis, chemical production, or refinery operation
- Development of instrumentation and controls for fluidized-bed and transport reactors.

During early conceptualization of the GPDU, an IGCC commercial system economic study projected minimal cost and performance differences between low-velocity HGD fluid beds and fixed or moving beds. The study also showed that costs could potentially be reduced by higher fluidization velocities and by regeneration schemes employing minimal undiluted air. Transport reactors potentially offered additional installation and operating cost savings relative to fluid bed reactors because of higher cross-sectional throughputs and lower sorbent inventory requirements. Based on these considerations and initial encouraging results from small-scale transport reactor testing, higher velocity fluidization regimes and transport reactor provisions were incorporated into the GPDU design. Shakedown is expected to begin in the fall of 1999 and be completed in 2000 (Tennant and Bissett 1999).

## 3. Related Developments in Sulfur Control in the U.S.

In addition to the sorbent and desulfurization reactor development, advanced processing schemes are being investigated with the following objectives.

- Direct Sulfur Recovery Process (DSRP) being developed by RTI to catalytically reduce $SO_2$ produced during regeneration of the sorbent into elemental sulfur using a small slipstream of coal gas (Portzer et al. 1998).
- One-step regeneration to produce elemental sulfur rather than $SO_2$ during regeneration . Two processes are being investigated: one at RTI called Advanced Hot Gas Process (AHGP) and one at Louisiana State University (LSU) by Professor Douglas Harrison (Harrison et al. 1998).
- Use of hot-gas desulfurization sorbents for non-IGCC applications.

The DSRP is an efficient process that converts up to 99 percent of the $SO_2$ produced during regeneration to elemental sulfur. However, for each mole of sulfur, this process requires 2 moles of reducing gas ($H_2$ + CO). This represents a small energy penalty in the process. To reduce this energy penalty, one-step regeneration processes are being developed.

The AGHP in which elemental sulfur is being produced during regeneration is described in detail in a paper presented in this conference by Dr. Santosh Gangwal. The one-step regeneration process developed by LSU involves a cerium oxide sorbent that is not a very good $H_2S$ getter. However, it is very selective in oxidizing the sulfide to elemental sulfur. The research examined the possibility of a second generation synthesis gas desulfurization process in which elemental sulfur is produced directly during sorbent regeneration. The concept involves desulfurization using $CeO_2$ and regeneration of sulfided sorbent, $Ce_2O_2S$, using $SO_2$ to produce elemental sulfur directly. No significant side reactions were observed and the reaction was quite rapid in the temperature range 500° to 700°C. Elemental sulfur (as $S_2$) in concentrations as large as 20 mol% was produced (Harrison et al. 1998).

Limitations of the cerium sorbent process were found, including high temperature and highly reducing gases such as those produced by the Shell gasifier being required to achieve high sulfur removal efficiencies. In integration with the Shell gasifier, the $CeO_2$ sorbent could achieve 1 to 5 ppmv $H_2S$ concentrations prior to breakthrough. Good sorbent durability has been demonstrated in 25-cycle testing. No measurable loss of sulfur capacity or reactivity was observed through 58 consecutive days of cycling between reducing and oxidizing conditions.

Use of hot-gas desulfurization sorbents for non-IGCC applications is being widely investigated. The RVS-1 sorbent, originally developed for moving-bed applications, has recently been used to desulfurize a synthesis gas produced by partial oxidation of distillate fuel by McDermott Technology, Inc. (MTI). MTI is developing a process for using this distillate fuel in a proton exchange membrane (PEM) fuel cell aboard a ship. This sorbent exhibited excellent performance in reducing the $H_2S$ level to <10 ppmv with a synthesis gas containing 36 vol% steam (Turk and Gupta 1998). Similarly, this sorbent has been investigated for desulfurizing a synthesis gas produced by gasification of biomass. In such a system, synthesis gas will be fed to a molten carbonate fuel cell (MCFC) for production of electricity. The EX-S03 sorbent developed for transport reactor applications has been investigated for desulfurization of sour natural gas.

In addition to $H_2S$ removal from synthesis gas, these sorbents are equally effective in removing COS. A series of tests done at RTI on the RVS-1 sorbents show that this sorbent was capable of reducing the COS content of feed from 200 to <2 ppmv. The presence of $H_2S$ in the feed had no effect on the performance of the sorbent for COS removal. Following the sulfidation with COS, the sorbent was successfully regenerated, and in subsequent cycles, the sorbent exhibited comparable performance to that of the previous cycle for $H_2S$ and COS absorption.

## 4. Desulfurization Work in Asia and Turkey

This section describes the R&D work being done on hot-gas desulfurization in Korea, China, Japan, and Turkey. This review is based on the published papers and personal communications with various researchers in these countries.

Korea Electric Power Research Institute (KEPRI) was involved in implementing a number of R&D projects related to the IGCC technology. One of the programs was to develop a HTHP desulfurization process and sorbent. A 3 in. ID bench-scale unit (BSU) test reactor was installed and demonstrated at KEPRI. Testing was conducted to address sorbent performance and durability issues with iron ores and zinc titanates. Efforts were also made to produce zinc titanate sorbents using a spray-drying technique with a variation of organic and inorganic binders. During 1998, the BSU reactor was modified to attach a riser; successful start-up and scaling parameters for the unit were documented for the fluid-bed or transport reactor in cold flow mode. KEPRI successfully developed a spray-dried zinc oxide-based ZAC series sorbent whose physical properties met the requirements for a transport reactor (i.e., semispherical shape, 100μm size, over 90 percent attrition resistant, and >15 wt% TGA sulfur loading). A ZAC-4N sorbent, in which ZAC-4 is impregnated with NiO, was tested

through 10 cycles at 500°C and 7 atm and showed no severe degradation from its fresh properties (KEPRI, 1998).

Various organizations within the Peoples' Republic of China have conducted some meaningful research. At the Institute of Coal Chemistry, Chinese Academy of Sciences, researchers have studied copper oxide sorbents and the effects of particle size and interaction of support materials on performance. It was observed that with a decrease in particle size from 625 to 142 nm, surface area increased fivefold and sulfur capacity improved by 12 percent. Additionally, impregnation of CuO on $Al_2O_3$ support lengthened the breakthrough time. In evaluating other support materials such as zirconia, titania, and 13X-Zeolite, it was found that sulfur-capacities relationships were $CuO < CuO/Al_2O_3 < CuO/13X\text{-}Zeolite < CuO/TiO_2 < CuO/ZrO_2$ (Hou et al. 1997).

Beijing Research Institute of Coal Chemistry has been developing the SMOVEN process for hot-gas desulfurization since 1993. As shown in Figure 6, the SMOVEN process features sulfidation in an entrained bed and regeneration in a low velocity fluid-bed or moving-bed reactor with sorbent recirculation. A desulfurizer process development unit was integrated with a small-scale fluid-bed gasifier and operated at 15$m^3$/h coal feed. The circulation of sorbent between the sulfidation and regeneration reactors was found to be stable and easy to control. The $H_2S$ concentration of 4,500 to 9,000 ppmv in inlet coal gas stream was reduced to <20 ppmv between 550° and 650°C and 0.7 atm. The sulfided sorbent was smoothly regenerated in the low-velocity fluid-bed reactor and the moving-bed operation mode. Regeneration tests with either air or oxygen were proved to be successful. The feasibility and operability of the SMOVEN process has been principally verified (Wanwang et al. 1997).

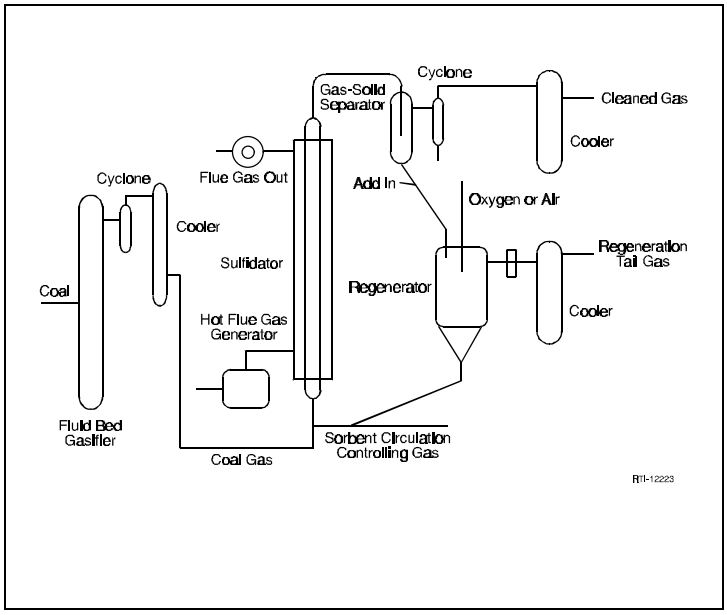


**Figure 6. Schematic of the SMOVEN Process.**

Chunhu et al. (1997a) at the China's Taiyuan University of Technology have examined methods to reduce sulfur species from 3 to 80 ppmv using wet desulfurization processing to as low as 0.5 to 1 ppmv. They have devised a three-stage process for

low-temperature desulfurization. The first and third beds use absorption of $H_2S$, COS, and $CS_2$ via nanometer-sized iron oxide particles and modified activated carbon with organic amine, respectively. The intermediate stage employs an alkali promoted, modified $\gamma$-$Al_2O_3$ hydrolysis catalyst. Operation is carried out at 40° to 120°C. Taiyuan University researchers also completed an analysis of hot-gas cleanup with respect to their IGCC systems in China. They surveyed the past 20 years of desulfurization literature in sorbent materials and reactor configurations. They concluded that (a) a temperature range of 530° to 650°C, (b) two stages of bulk followed by fine desulfurization using inexpensive iron oxide and zinc ferrite, and (c) a moving-bed configuration would be most beneficial for integration with available IGCC systems and the industrial situation in China (Chunhu et al. 1997b).

In Japan, Mitsubishi Heavy Industries (MHI) tested a fixed-bed dry-gas cleanup system consisting of an iron oxide honeycomb and a sulfur recovery process. From published papers, MHI reported that a synthesis gas containing 570 to 670 ppmv of sulfur was desulfurized to 20 to 50 ppmv using this honeycomb (Ohta 1997). No further information is available on the current status of this technology.

Another major R&D project on high temperature desulfurization in Japan was conducted by Ishikawajima-Harima Heavy Industries (IHI). IHI's initial work involved use of iron oxide sorbent; however, iron oxide was not able to reduce the sulfur content of coal gas to <20 ppmv (Sugitani et al. 1989). IHI had participated in both the Yubari (40 tpd) and Nakoso (200 tpd) projects, in which they had used iron oxide as a hot-gas desulfurization sorbent. Later work done by IHI involved use of ZnO-based sorbents (Yasui 1997).

Japan's Agency of Industrial Science and Technology/MITI completed their 4-year study of the feasibility of an IGCC plant based on an air-blown gasifier. The hot-gas cleanup systems, as evaluated at Nakoso, were chosen to be replaced by cold-gas cleaning principally because (a) regulations on flue-gas emissions had become more stringent during Nakoso pilot-plant testing and (b) process reliability took priority over higher efficiency. The hot-gas cleanup systems tested exhibited plugging and agglomeration in downstream components. Though more costly, an amine-based acid gas solvent process was chosen as being commercially available, reliable, and effective. This process produces gypsum with the high concentrations of $H_2S$ produced during the regeneration of amine. The gypsum is in great demand in the Japanese market (Wada 1999; Watanabe 1999).

At the Middle East Technical University, Ankara, Turkey, research continues under supervision by Dr. Aysel Atimtay, where a novel sorbent was developed by loading zinc-iron-vanadium oxide salts onto a stabilized silica support. The zinc ferrite and vanadium-promoted sorbents were sulfided with a 5,000 ppmv $H_2S$ gas mixture at atmospheric pressure and temperatures of 600° to 700°C. The results showed that the vanadium increased initial reaction rates at all temperatures and that zinc losses were decreased at high temperatures (Derinoz 1998).

## 5. Future Trends

High-temperature removal of reduced sulfur species from synthesis gas produced by gasification of carbonaceous feedstocks has for the most part moved through to the initial demonstrations at large-scale facilities. In the United States, sorbent materials and the reactor designs in which they will be used have been fairly well-matched. Current promulgated emission standards are being met. Operational considerations such as long and effective life expectancy of sorbents at an economical price are being achieved. The definition of an IGCC facility is changing to that of a multiple- product slate producer. It is expected to not only provide electric power via combustion turbines, but also be a source for synthesis gases readily useful as precursors for chemicals or fuels production, generate electric power by way of fuel cells technology, and even be a source of hydrogen for integration into hydrogenation processes in refineries. With this shift, an extreme leap of innovation and ingenious strategies must be applied to meet synthesis gas specifications for such IGCC plants of the future. Sulfur control methods must now head toward achieving parts-per-billion levels while still maintaining consideration for cost effectiveness and without adversely effecting the ever-increasing IGCC demand for overall system efficiency.

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